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Producing Chlorination-Grade Feedstock From Domestic Ilmenite—Laboratory and Pilot Plant Studies

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	kg/min	kilogram per minute
°C	degree Celsius	kV•A	kilovolt ampere
cm	centimeter	kW	kilowatt
cm^3/min	cubic centimeter per minute	lb	pound
ft	foot	lb/h	pound per hour
ft^3/min	cubic foot per minute	L/min	liter per minute
g	gram	min	minute
gal	gallon	mL	milliliter
g/L	gram per liter	mm	millimeter
g/min	gram per minute	pct	percent
h	hour	st	short ton
h/d	hour per day	V	volt
in	inch	wt pct	weight percent
kg	kilogram	yr	year

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By G. W. Elger,[1] J. B. Wright,[2] J. E. Tress,[2]
H. E. Bell,[2] and R. R. Jordan[3]

ABSTRACT

The Bureau of Mines investigated the conversion, at both laboratory and pilot plant scale, of a low-grade ilmenite to chlorination-grade feedstock that could substitute for imported rutile used to produce titanium tetrachloride. The concentrate was derived from the Tahawus, NY, lode deposit of ilmenite-magnetite in rock that contains anorthosite and gabbro.

Charges of the ilmenite concentrate, containing 46.6 wt pct TiO_2 blended with soda ash, were carbothermically reduced in an electric arc furnace, which separated most of the iron and left a high-titanium slag. However, the slag contained Ca, Mg, and Mn constituents that rendered the material unsuitable for continuous chlorination by causing plugging problems. After being ground and pelletized, the slag was reacted with SO_2 and air at 700° to 900° C, which selectively converted the harmful impurities to soluble compounds that were removed in a subsequent water or dilute HCl leach.

In laboratory tests, the combined levels of harmful impurities were decreased from 5 to as low as 0.5 wt pct in leached slags. In pilot plant tests, leached slags sulfated at a rate of 10 lb/h averaged 85.5 wt pct TiO_2 with pertinent impurity levels averaging 1.86 wt pct. The leached slag was successfully chlorinated in a laboratory fluidized-bed reactor at 950° C to extract titanium as $TiCl_4$.

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INTRODUCTION

The United States depends upon imports to supply most of the rutile and up to 70 pct of the ilmenite and titanium slag requirements for the manufacture of TiO_2 pigments, titanium metal, and welding rod coatings (1).[4] To help assure an adequate supply of titanium raw materials to meet national economic and strategic needs, the Bureau of Mines undertook research to devise new technology that efficiently and economically recovers titanium from the abundant low-grade titaniferous materials in massive rock deposits.

Approximately 92 pct of the titanium raw materials consumed is used in the domestic production of TiO_2 by either chloride or sulfate process technology. The other 8 pct is consumed in producing titanium metal and other products. Sulfate process plants, which produce less than 30 pct of the TiO_2, are based on the dissolution of ilmenite and/or titanium slag in sulfuric acid. Iron sulfate is separated by crystallization, and the remaining solution is diluted to precipitated hydrated TiO_2, which is calcined to TiO_2. Chloride process technology, which is environmentally cleaner and generates less waste materials than the older sulfate process, accounts for more than 70 pct of the domestic production of TiO_2. In chloride process plants, rutile or a substitute feedstock such as ilmenite is reacted with chlorine and coke under reducing conditions in fluidized-bed reactors operating at 950° to 1,150° C to produce $TiCl_4$. The crude $TiCl_4$ is purified and either oxidized to TiO_2 or reduced to titanium metal by reaction with magnesium or sodium.

Although titanium-bearing minerals are found in sand- and rock-type deposits throughout the world, the current demand for titanium raw materials to produce TiO_2 and titanium metal by chloride process technology is primarily satisfied by two mineral sand concentrates (2) rutile, which contains about 95 wt pct TiO_2, and ilmenite ($FeO \cdot TiO_2$), which contains more than 55 wt pct TiO_2. The United States has only limited reserves of these titanium minerals in sand deposits (1), but has abundant quantities of lower grade ilmenite and other titaniferous minerals in massive rock deposits, as shown in figure 1. Unfortunately, these lower grade titanium raw materials contain Ca, Mg, and Mn oxide impurities that render them unsuitable as feedstock for continuous chlorination in fluidized-bed reactors. The troublesome impurities form high-boiling-point liquid chlorides, which accumulate to form solid masses with the coke and mineral particles in the bed and eventually cause loss of fluidization in the reactor.

The selection of chlorination feedstock used to produce $TiCl_4$ is dependent on several factors, including cost, availability, TiO_2 content, and impurity levels. With increased consumption of rutile in $TiCl_4$ production, the price of the concentrate has risen from about \$45/st in 1961 to \$490 in 1985 (3); only about \$100/st of the increase was due to inflation. Moreover, world reserves of rutile are limited. To minimize feedstock costs, one major domestic TiO_2 producer chlorinates an ilmenite-rutile-leucoxene feedstock that contains about 62 wt pct TiO_2. Direct chlorination of ilmenite generates large quantities of iron and other metal chloride wastes that present potential disposal and pollution problems. Rutile chlorination

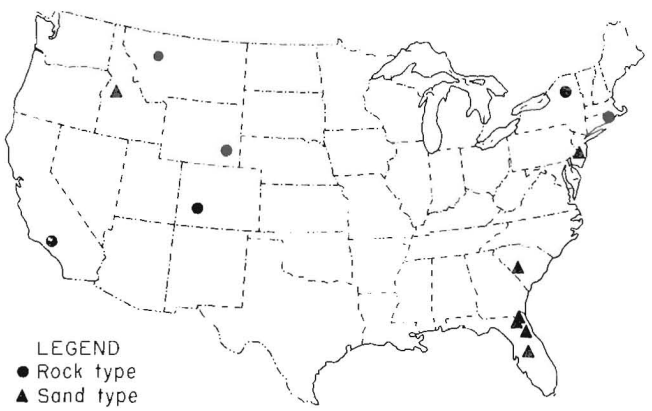

FIGURE 1. - Titanium deposits in the United States.

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

generates 0.12 st of waste whereas ilmenite chlorination generates about 1.5 st of waste for each ton of $TiCl_4$ produced (4). In all instances, chlorination feedstock must contain relatively low levels of impurities that inhibit continuous operation. The upper limit for these impurities in chlorination feedstock is reported to be 1.0 wt pct MgO and 0.2 wt pct CaO (5).

Increasing costs of rutile and concerns about metal chloride wastes have prompted several domestic $TiCl_4$ producers to import cheaper nonrutile raw materials, containing 85 to 92 wt pct TiO_2, that have been upgraded from ilmenite sands according to the four principal processes described by Kahn (4). Three of these processes involve solid-state reduction of iron oxides in ilmenite to either ferrous oxide or metallic iron, followed by acid leaching or oxidizing the iron product from the TiO_2. The resultant product is known as synthetic rutile or upgraded ilmenite. In the fourth process, ilmenite concentrate is carbothermically reduced using a coal reductant in an electric arc furnace to separate most of the iron as salable pig iron and to produce titanium slag. Richards Bay Minerals in the Republic of South Africa produces about 440,000 tons per year of 85-wt-pct-TiO_2 slag from ilmenite concentrate from beach sands. It is reported to be suitable for either chloride or sulfate process TiO_2 manufacture (4).

To date, no viable process has been developed to produce suitable feedstock for fluidized-bed chlorination from low-grade titaniferous rock materials. In Canada, Quebec Iron and Titanium Corp. (QIT) employs an electric arc smelting process (6) that converts Allard Lake Ilmenite rock concentrate grading about 35 wt pct TiO_2 to pig iron and about 900,000 tons per year of slag that contains approximately 72 wt pct TiO_2, 13 wt pct FeO, with 6 wt pct CaO + MgO and 0.2 wt pct MnO impurities. QIT slag, with its relatively high level of harmful impurities, is used mainly as feed in sulfate process TiO_2 manufacture. Bureau investigators (7) evaluated 18 domestic titaniferous materials by electric arc smelting to produce metallic iron and titanium slags for $TiCl_4$ production. They found that the resulting slags contained impurity levels too high for continuous chlorination.

To meet a need to enhance the utilization of domestic titaniferous rock materials as sources of chlorination feedstock for $TiCl_4$ production, the Bureau developed a sulfation-leaching technique to decrease the troublesome impurity levels in titanium slag before chlorination. In a bench-scale investigation, a New York ilmenite rock concentrate of about 46 wt pct TiO_2 was upgraded successfully to a slag product that contained about 88 wt pct TiO_2, with less than 0.07 wt pct CaO, 0.3 wt pct MgO, and 0.03 wt pct MnO impurities (8).

The sulfation-leaching technique involves selective conversion of the MgO, CaO, and MnO impurities in titanium slag to water-soluble forms by reaction with SO_2-O_2 mixtures in the presence of a sulfation promoter. After cooling, the sulfated slag is ground, and the ground material is leached in either water or dilute HCl solution to remove the soluble impurities. Effective conversion of MgO and MnO constituents in the slag to rutile is dependent on the oxidation of the major titanium-bearing phase having the pseudobrookite-type structure (9-10). The pseudobrookite-type phase forms in slag smelted at low O_2 partial pressures and contains impurities such as Fe, Mg, Mn, and Al, which substitute for divalent and trivalent titanium oxides (11). When Ti_2O_3 and TiO are oxidized to TiO_2, the pseudobrookite-type structure is converted to rutile, which has a low solubility for the above impurities (12).

Results of previous bench-scale tests indicated that efficient impurity sulfation depends on the presence of a sulfation promoter in titanium slags of low iron content (13). The mechanisms of the sulfation reactions and the role of the promoter were beyond the scope of the present investigation. It was found that additives such as soda ash and sodium sulfate promoted impurity sulfation (13). Subsequent testing demonstrated that soda ash could be added with the ilmenite charge in the smelting step, where the additive lowered the viscosity of

titanium slags having FeO contents below 6 wt pct. In commercial smelting of ilmenite, 10 to 13 wt pct FeO is left in the slag to preserve fluidity. Because titanium slags with less than 6 wt pct FeO responded most satisfactorily to impurity sulfation, soda ash was added with the ilmenite-coke charges to maintain slag fluidity in the absence of the higher FeO content. A phase diagram of the Na_2O-TiO_2 system suggests that slag containing about 6 wt pct Na_2O exhibits a liquidus temperature of approximately 1,575° C (14). Previous investigators reported that soda ash reduces the slag viscosity and decreases the electrical energy requirements for smelting ilmenite (5).

This report discusses the results of bench-scale tests made to produce a potential chlorination-grade titanium slag from a Tahawus ilmenite concentrate derived from a massive rock deposit mined in New York State. Figure 2 shows a schematic diagram of the overall process, including the chlorination of slag to produce $TiCl_4$. Ilmenite charges blended with coke and soda ash were smelted in an electric arc furnace to remove most of the iron as metallic iron and to prepare slags with different FeO levels for sulfation-leaching tests. Pelletized and ground slag charges blended with and without an Na_2SO_4 additive were reacted with equal proportions of SO_2 and O_2. Three series of static-bed tests were performed to determine the effects of FeO content of slag, sulfation temperature and time, and Na_2SO_4 addition on the impurity removal from leached slags. After cooling, the sulfated slags were ground and leached with water or a 1-wt-pct-HCl solution to remove the impurities, and the Na_2SO_4 was added as a sulfation promoter.

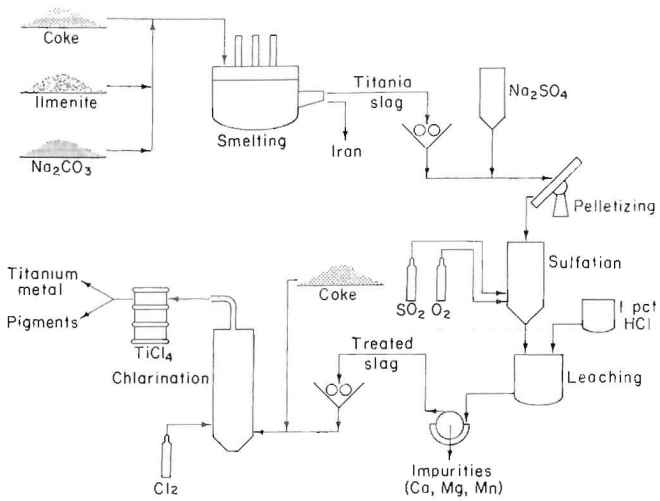

FIGURE 2. - Processing of ilmenite.

These encouraging results prompted the Bureau to investigate processing of ilmenite rock material by electric arc furnace smelting and sulfation-leaching techniques in pilot-scale equipment. This report also discusses the preparation, treatment, and chlorination of titanium slag from New York ilmenite, using a 1-st-capacity electric arc furnace and a continuous sulfation reactor operating at 10 to 20 lb/h of slag.

LABORATORY STUDIES

SMELTING TESTS

Starting Materials

The ilmenite concentrate used to prepare titanium slag was obtained from a massive deposit of primary ilmenite-magnetite minerals in rock containing anorthosite and gabbro. Ilmenite concentrate produced from this deposit, located near Tahawus, NY, formerly was used as feedstock for a domestic sulfate process TiO_2 plant that closed owing to world economic conditions and declining markets. This material was selected for this investigation because it was representative of low-grade titaniferous rock material available from the largest domestic titanium reserve.

The sample of ilmenite concentrate contained 46.6 wt pct TiO_2 along with the oxides of Fe, Mg, Si, Al, and lesser amounts of Ca and Mn as impurities, as shown by the chemical analysis given in table 1. Spectrographic data indicated the ilmenite sample also contained trace amounts of Co, Ni, and Cu.

The composition of the Tahawus ilmenite is similar to that of Allard Lake ilmenite rock material smelted by QIT in

TABLE 1. - Chemical composition of ilmenite concentrate

Constituent	wt pct
TiO_2	46.6
FeO	35.7
Fe_2O_3	12.4
MgO	2.1
SiO_2	1.6
Al_2O_3	1.0
CaO	.3
MnO	.3
V_2O_5	.07

Sorel, Quebec, Canada. Mineralogical examination of the Tahawus concentrate revealed that the ilmenite grains were intergrown with magnetite and ferromagnesium silicates. Small amounts of the accessory minerals garnet, pyroxene, and feldspar and trace amounts of pyrite and calcite also were present.

Charge Preparation

For each smelting charge except one, 22.7 kg of ilmenite was blended with 2.7 kg of petroleum coke, 2.0 kg of soda ash, and 0.3 kg of bentonite binder. Petroleum coke was chosen as the reductant because of its high fixed-carbon content (89.1 wt pct) and low ash (1.1 wt pct). The coke provided carbon usually equivalent to 120 to 130 pct of the stoichiometric requirement to produce metallic iron. In one test, 4.4 kg of petroleum coke was used, which was equivalent to 200 pct of stoichiometric carbon requirement. The furnace charge mixtures were pelletized with water on a rotating-disk pelletizer, and the 1.5-cm-diam pellets were dried in an oven at 120° C.

Equipment

An electric arc furnace with a nominal capacity of 23 kg and powered by a 1,000-A single-phase arc welding transformer was used for the smelting tests. The furnace was equipped with two carbon electrodes and a hot-ram carbon-lined shell having an inside diameter of 30 cm. The furnace normally was operated at a current of 900 A and 60 V, which provided a power input of approximately 55 kW.

Test Procedures

Approximately 15 pct of the pelletized charge was placed on the furnace hearth, and the electrode tips were moved toward each other to start an arc. As soon as the charge material melted and formed a molten pool, the electrodes were moved farther apart. The remainder of the charge was added continuously at a rate of approximately 0.3 kg/min. When the entire charge was melted and a bath temperature of 1,575° to 1,650° C was attained, the contents of the furnace were tapped into a slag pot. After cooling, the slag and metal were separated, and the slag was ground and sampled for chemical analyses.

Results

Chemical analyses of 10 separate slags produced with different FeO contents during the smelting tests are shown in table 2. The FeO content of these slags ranged from 3.3 to 14.9 wt pct. The slag samples contained combined levels of CaO, MgO, and MnO impurities near 5 wt pct, well above the acceptable levels for chlorination feedstock.

TABLE 2. - Partial chemical analyses of titanium slags smelted from low-grade Tahawus ilmenite concentrate[1]

Test	Constituent, wt pct					
	Total Ti	FeO	CaO	MgO	MnO	Na_2O
1..	39.4	14.9	0.81	3.66	0.53	4.22
2..	51.6	3.29	1.15	3.60	.37	2.16
3..	47.8	4.35	.85	3.65	.44	2.30
4..	45.1	5.79	.57	2.52	.34	6.54
5..	36.2	11.40	.55	3.02	.48	9.60
6..	47.1	5.29	.60	3.57	.36	5.14
7..	48.2	4.97	.71	3.55	.39	4.26
8..	47.3	4.40	.84	2.98	.27	3.28
9..	44.9	5.96	.59	3.48	.43	5.35
10..	47.1	4.73	.71	3.33	.43	4.00

[1]Sulfur content ranged from 0.6 to 0.9 wt pct.

SULFATION STUDIES IN A STATIC BED

Three series (A, B, and C) of sulfation tests were performed to convert the CaO, MgO, MnO, and Na_2O constituents in titanium slag to soluble forms using SO_2-O_2 mixtures. For the three series of tests, the operating conditions investigated included sulfation temperature and time, proportion of Na_2SO_4 added as a sulfation promoter, and FeO content of slag. Slags from smelting tests 2 and 3 were used for series B and A, respectively, to provide a sufficient number of charges for sulfation. Slags containing from 3.3 to 14.9 wt pct FeO from the eight smelting tests were used for series C.

Charge Preparation

The Na_2SO_4 promoter and the slags from all smelting tests listed in table 2, except heats 7 and 8, were ground separately to pass through a 65-mesh screen. Each ground slag was blended with 1 wt pct bentonite as a binder, and 0 or 10 wt pct Na_2SO_4 was added. Each blended charge was pelletized with water on a disk pelletizer. Minus 10- plus 20-mesh pellets prepared for series A and 0.6-cm-diam pellets prepared for series B and C were dried in an oven at 110° C before being used. The smaller pellets were necessary for use in the smaller reactor.

Sulfation Tests

Series A

The initial series of tests was made to study the effects of sulfation temperature and time on the formation of soluble impurities in titanium slag derived from smelting heat 3. This slag was selected because it had a composition most closely approximating the slag to be used in future large-scale work.

Apparatus

The 51-mm-diam reactor, shown in figure 3, was fabricated from clear quartz and consisted of two main sections. The pelletized charge was contained in the upper section of the reactor, while the incoming reactant gases were preheated in the lower section.

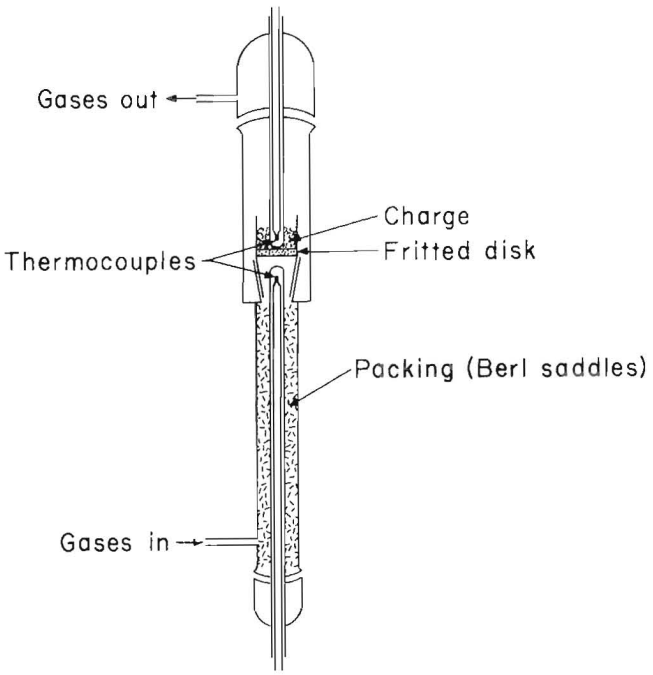

FIGURE 3. - Apparatus for slag sulfation in series A tests.

The charge was supported on a coarse, fritted quartz disk that formed the bottom of a crucible. The crucible, in turn, was attached to a ground joint. The mating portion of the joint was sealed to the reactor inner wall so that the gases were forced to pass through the fritted disk and, subsequently, the pelletized charge. A thermocouple well was inserted from the top of the reactor so that its tip was buried in the charge. A hook also was fitted to the well for inserting and withdrawing the charge crucible. Another thermocouple well was inserted upwards from the bottom of the reactor so that its tip was just below the charge support. The annular space between the well and the reactor wall was packed with Berl saddles to improve heat transfer and mixing of the incoming reaction gases.

The SO_2 and O_2 were metered individually by means of rotameters. Prior to being discharged to the atmosphere, exit gases were scrubbed with a caustic solution in a packed column to remove the SO_2 and SO_3 gases.

The entire reactor was heated electrically in a two-zone tube resistor furnace that allowed independent control of the temperature of each main reactor section. This made it possible to maintain the reactant gases at precise temperatures just prior to contacting the charge.

Test Procedures

Each test in series A was conducted in the following manner. A 10-g portion of the pelletized mixture was weighed and transferred to the charge crucible. The crucible was positioned in the reactor, and the system was flushed with Ar to prevent any premature reaction while the reactor was being preheated to the desired temperature. When the temperature stabilized, the Ar flow was stopped and equal flows of SO_2 and O_2 were started. During the test period, the flow rates of gases were monitored and maintained at 110 cm^3/min each to provide a minimum of 100 pct excess of the stoichiometric amount of gases required to sulfate the impurities. Reaction temperatures of 700°, 800°, or 900° C were maintained while sulfating slag charges for either 1/4, 1/2, 1, 2, of 4 h. At the end of the test, the hook on the upper thermocouple well was used to raise the charge crucible to the upper end of the reactor, where the charge was allowed to cool rapidly in an atmosphere of a 1:1 mixture of SO_2 and Ar to prevent possible decomposition of the sulfated products. Subsequent testing, however, showed negligible differences when the charge was cooled in other atmospheres, including air. After cooling, the sulfated pellets were weighed, ground to minus 65 mesh, and sampled for analysis before leaching.

Series B and C

Tests in series B were performed to determine the effects of temperature, time, and proportion of Na_2SO_4 added on the formation of soluble impurities in slag from smelting heat 2 (table 2). The series was conducted according to a partial factorial design. Temperatures of 700° and 900° C, reaction times of 1 and 4 h, and Na_2SO_4 additions of 0 and 10 wt pct defined the variables, and all tests were replicated.

Series C tests were made to study the effects of FeO content of slag and sulfation temperature on impurity levels in leached slags. The eight slags with FeO contents of up to 14.9 wt pct contained 10 wt pct Na_2SO_4 additive and were subjected to sulfation at temperatures of 700°, 800°, and 900° C for 2 h.

Both test series were scaled up to 50-g charges of pellets, which required the use of a different reactor than that used for series A. The purpose was to determine if a larger charge of sulfated pellets would exhibit a tendency to form agglomerates in a fixed bed owing to sticky reaction products coating the surfaces of the pellets.

Apparatus

The reactor (fig. 4) used for sulfating 50-g pellet charges was fabricated from clear quartz and was divided at the midpoint by a slotted support for the pellet charge. Each end of the 51-mm-diam reactor tube was fitted with a ground joint. A gas inlet was provided at the top, and an exit tube and liquid trap were attached at the bottom. The pelletized charge was placed on a bed of quartz wool on the slotted support. A tube furnace with electrical resistance elements was used to heat the sulfation reactor. Flowrates of the incoming gases were measured with rotameters, and the exit gases passed through a packed column where they were scrubbed with a caustic solution to remove SO_2 and SO_3.

Test Procedures

The following procedure was employed to sulfate pellet charges in series B and C. A weighed, 50-g portion of the pelletized slag charge was loaded into the reactor, and the system was flushed with Ar while the reactor was heated to the desired temperature. When the temperature stabilized, equal volumes of SO_2 and O_2 were introduced at a total flowrate of 200 cm^3/min. At the completion of the test, the gas flows were stopped, the system was sealed, and the sulfated charge was

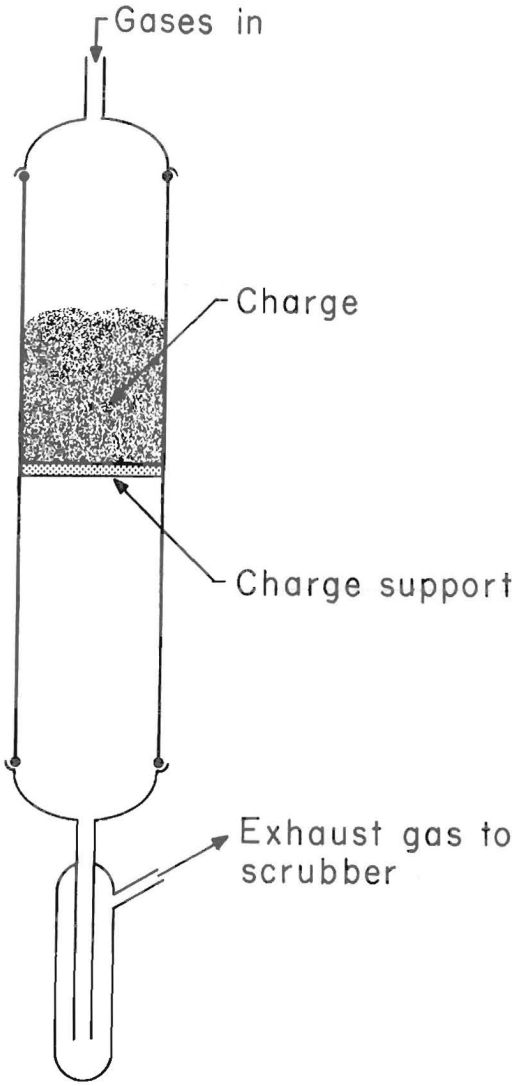

FIGURE 4. - Apparatus for slag sulfation in series B and C tests.

allowed to cool to ambient temperature before removal from the reactor. Previous testing had revealed that the sulfated charges could cool in the furnace overnight without influencing the leachability of the impurities. After weighing, the cooled, sulfated charge was sampled for chemical analysis.

Removal of Soluble Impurities

The following procedure was utilized to determine the percentage of soluble impurities formed in sulfated slags during the three series of tests. A 5-g sample of the ground, sulfated slag was leached in 100 mL of a 1-pct-HCl solution with

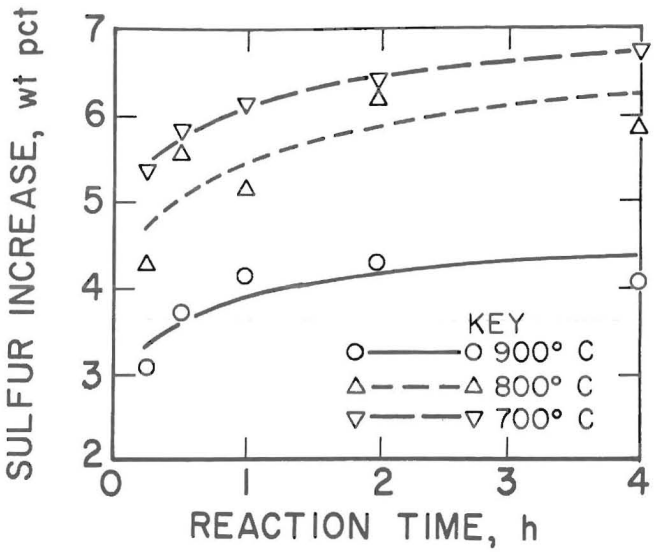

FIGURE 5. - Effect of sulfation temperature and time on the sulfur increase in titanium slag 3 (table 2) containing 10 wt pct Na_2SO_4 additive.

constant stirring for 1 h at ambient temperature. In the leaching step, a 1-wt-pct-HCl solution rather than water alone was used to prevent hydrolysis of the dissolved constituents in the leach liquor samples used for analyses. Moreover, results indicated that the solubility of $CaSO_4$ was about 7 g/L in the HCl solution, compared with 2.5 g/L in water. However, in industrial practice, water leaching probably would be preferred because the waste liquor with a pH of approximately 4.5 could be easily neutralized with limestone.

The slurry was filtered, and the slag was repulped twice for 5-min periods with additional acid. After the final filtration, the leached slag was dried. The initial filtrate and wash filtrates were measured and combined. Samples of both slag and leach liquor were analyzed to determine the percentage of impurities removed during the leaching operation.

Results and Discussion

For series A, the curves in figure 5 depict the sulfur increase in slag charges sulfated at 700°, 800°, or 900° C for reaction times of 1/4, 1/2, 1, 2, or 4 h. The data show that more than 70 pct of the increase in sulfur content was attained during the initial 15-min reaction

period at each of the temperatures investigated. The sulfur increase was measured by comparing chemical analyses of slag charges before and after sulfation and adjusting for any sulfur added as Na_2SO_4.

The sulfur increase during the 900° C test closely approximated the sulfur removed from the slag as soluble Ca, Mg, and Mn sulfates during the postsulfation leaching procedure. An examination of the three curves indicates that more sulfur was contained in the slag charges sulfated at 700° and 800° C than can be accounted for in the sulfation of the Ca, Mg, and Mn impurities. This suggests that other compounds, such as sodium pyrosulfate, may have formed at temperatures below 900° C. However, X-ray diffraction data did not confirm the presence of such a compound in sulfated slag samples.

The effects of reaction time and temperature on the removal of individual impurities from the leached slag are shown in figure 6. The curves in this figure were drawn using a regression analysis according to the general equation $y = a + b \ln x$. Typical chemical analyses of the pertinent impurities remaining in leached slag sulfated at 900° C for the above reaction times are shown in table 3. The increased FeO content of leached slag is due to the removal of the soluble impurities. The data indicate that efficient conversion of the harmful impurities to leachable forms was achieved in slag charges sulfated at 900° C using a minimum reaction time of 1/2 h. The sulfur constituent was readily removed from a slag charge sulfated for only 1/4 h. Examination of the curves in figure 6 reveals that Ca and Na were more easily removed and that reaction times of less

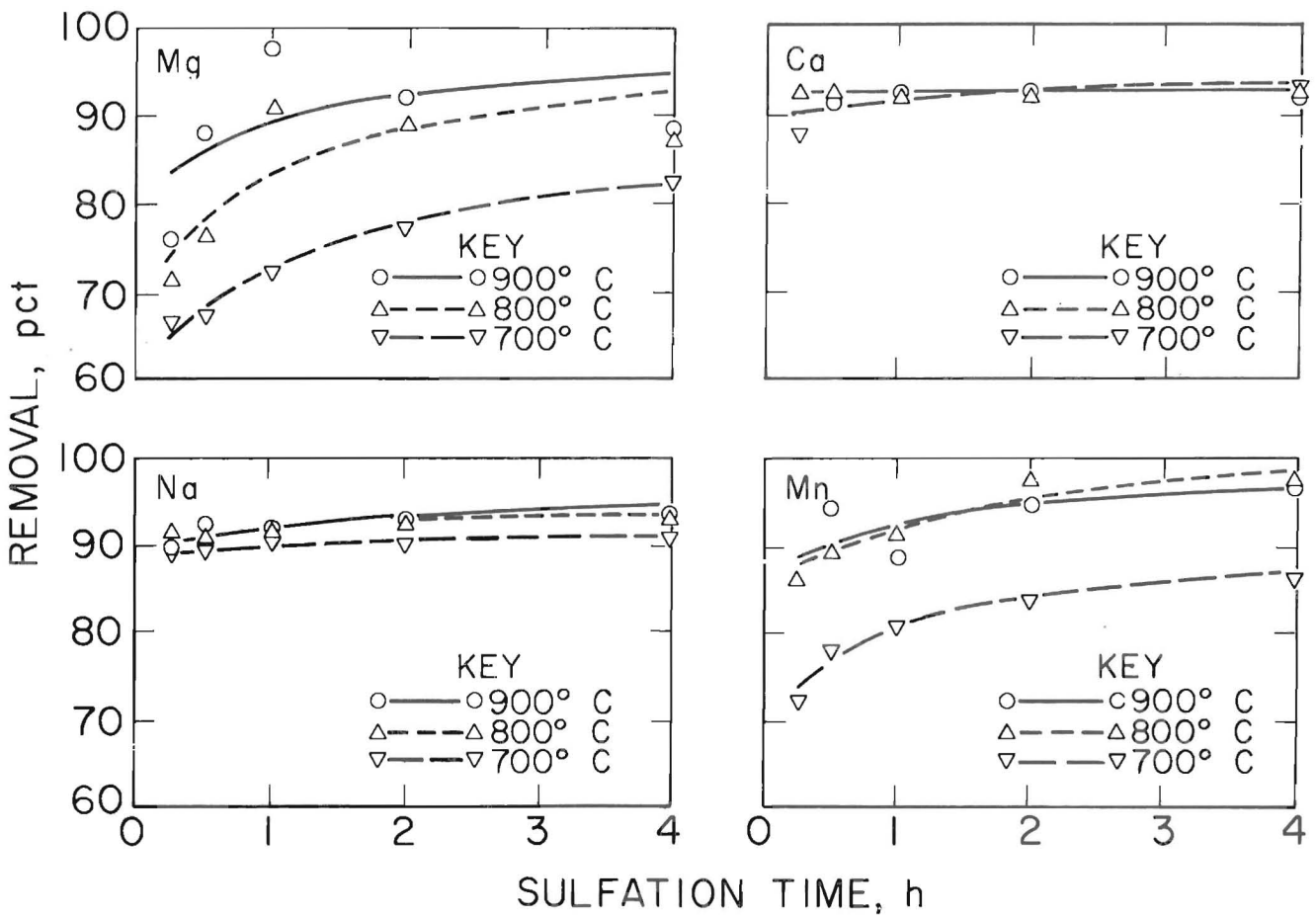

FIGURE 6. - Effect of reaction time and temperature on the removal of impurities from leached slag 3 (table 2) containing 10 wt pct Na_2SO_4 additive.

TABLE 3. -- Analyses of pertinent impurities in slag sulfated at 900° C and subsequently leached in a 1-wt-pct-HCl solution[1]

Time, h	Impurity, wt pct [2]					
	FeO	CaO	MgO	MnO	Na_2O	S
0.25	5.43	<0.07	0.93	0.06	0.40	0.21
.5	5.68	<.07	.43	.03	.22	.18
1.0	5.48	<.07	<.08	.05	.28	.19
2.0	5.53	<.07	.30	.03	.12	.17
4.0	6.17	<.07	.43	.01	.11	.17

[1]Slag of smelting test 3 contained, in wt pct, 4.35 FeO, 0.85 CaO, 3.65 MgO, 0.44 MnO, and 2.3 Na_2O.

[2]Shown as oxide equivalents, except for S.

than 1/4 h were sufficient to convert the compounds of these two elements to soluble forms. Compounds of Mn were less easily removed unless more time and higher sulfation temperatures were used. The data indicate that sulfating slag at 800° or 900° C for at least 2 h was needed to achieve nearly complete Mn removal. Magnesium compounds were the most difficult of the impurities to remove. Overall impurity removals were found to be directly proportional to sulfation temperatures, with a minimum required reaction time of 2 h.

For series B, table 4 summarizes the data that show the effects of sulfation temperature and time and proportion of Na_2SO_4 additive on the impurity removals from leached slag (smelting heat 2, table 2). The best overall impurity removal of 94.2 pct was achieved with leached slag sulfated at 900° C for 4 h in the presence of 10 wt pct Na_2SO_4. In the removal of the individual impurities, the same general pattern as observed in series A tests for the Ca and Mg impurities was noted for tests in series B. The added Na_2SO_4 exhibited the greatest effect on increasing the removal of Mn and Na compounds.

Results of the tests in series C are shown in table 5. The first six slags, which contained 5.96 wt pct or less FeO, responded the best to sulfation at 800° C and above. The troublesome impurity levels in the leached slags of smelting tests 2 through 9 (table 2) were well within the upper limits for acceptable chlorination feedstock. The other two slags, which had FeO contents of 11.4 and 14.9 wt pct, contained more than 1 wt pct MgO and 0.1 wt pct MnO and therefore did not sulfate as well as the leached products.

The influence of FeO on impurity sulfation in titanium slags may be attributed to the incomplete conversion of the pseudobrookite-type structure to rutile. X-ray diffraction and scanning electron microscopy data indicated that the Mg and Mn constituents in solid solution in the pseudobrookite-type phase of sulfated slag did not respond very effectively to sulfation. Webster and Bright (12) reported that substitution of impurity oxides such as those of Fe for divalent and trivalent titanium oxides in the crystal lattice tends to increase the stability of the pseudobrookite phase. Bureau investigators found that effective conversion of pseudobrookite to rutile was not achieved in Sorel slag that contained 13.3 wt pct FeO, and 20 to 30 pct of the titanium remained as pseudobrookite (10).

The reactions involved in slag sulfation are complex owing to the partitioning of the Ca, Mg, Mn, and Na constituents in the pseudobrookite-type, $Na_{0.23}TiO_2$, and silicate-type glass phases of slag. The role of the Na additive as a promoter of impurity sulfation has not been defined. Basic studies to identify reaction mechanisms and the role of the sulfation promoter are needed to make further improvements in operating procedures and to provide information on design of larger scale sulfation reactors.

No evidence of pellet agglomeration was noted when the static-bed sulfation was scaled up to 50-g charges. This is significant from the standpoint that the sulfated pellets do not stick together, which would make further scale-up to continuous sulfation a difficult operation.

LEACHING STUDIES

A series of tests was performed to acquire data that would aid in determining

TABLE 4. - Effect of Na_2SO_4 additive and sulfation temperature and time on impurity removal from leached slag[1]

Test	Sulfation temp, °C	Sulfation time, h	Leached slag analysis, wt pct[2]				Impurity removal, wt pct				
			CaO	MgO	MnO	Na_2O	CaO	MgO	MnO	Na_2O	Overall
NO Na_2SO_4 ADDITIVE											
1.....	700	1	0.08	1.81	0.09	0.25	91.7	52.1	76.9	86.9	72.2
2.....	700	1	.08	1.69	.08	.34	94.4	59.4	84.6	87.3	75.9
3.....	900	1	<.07	.95	.06	.18	>94.4	74.7	84.6	91.6	84.0
4.....	900	1	<.07	.91	.05	.15	>94.4	75.8	84.6	92.9	85.0
5.....	700	4	<.07	1.64	.09	.22	>94.4	56.8	76.9	90.0	75.2
6.....	700	4	<.07	1.66	.08	.23	>94.4	55.8	84.6	90.0	75.2
7.....	900	4	<.07	.81	.09	.09	>94.4	78.7	76.9	95.7	86.8
8.....	900	4	<.07	.73	.03	.12	>94.4	80.0	92.3	94.3	87.8
10 wt pct Na_2SO_4 ADDITIVE											
9.....	700	1	0.13	0.93	0.09	0.63	87.9	75.3	75.0	90.6	82.8
10.....	700	1	<.07	1.03	.05	.31	>93.8	72.4	90.9	96.0	84.8
11.....	900	1	<.07	.70	.04	.27	>93.9	81.6	91.7	96.2	89.1
12.....	900	1	<.07	.76	.03	.24	>93.8	77.5	90.9	96.1	87.1
13.....	700	4	<.07	1.06	.05	.26	>93.5	72.8	90.9	96.6	85.2
14.....	700	4	<.07	1.11	.04	.27	>93.5	71.6	90.9	96.4	84.6
15.....	900	4	<.07	.30	.03	.12	>93.8	91.7	90.9	98.5	94.2
16.....	900	4	<.07	.51	.01	.12	>93.8	86.9	96.4	98.5	92.4

[1]Slag made from ilmenite in smelting test 2 contained, in wt pct, 1.15 CaO, 3.6 MgO, 0.37 MnO, and 2.16 Na_2O as pertinent constituents before sulfation.
[2]Shown as oxide equivalents.

TABLE 5. - Effect of iron content and sulfation temperature on pertinent impurity levels in leached slags[1]

FeO content, wt pct	Slag test	Impurity levels at various sulfation temperatures, wt pct[2]												Impurity levels before sulfation, wt pct[2]		
		700° C				800° C				900° C						
		CaO	MgO	MnO	Na_2O	CaO	MgO	MnO	Na_2O	CaO	MgO	MnO	Na_2O	CaO	MgO	MnO
3.29	2	NT	NT	NT	0.23	<0.07	0.34	0.01	0.22	0.07	0.50	0.04	0.38	1.15	3.60	0.37
4.35	3	<0.07	0.53	0.04	NT	<.07	.54	.03	.14	<.07	.52	.04	.34	.85	3.65	.44
4.73	10	.10	.70	.05	.31	<.07	.35	.03	.21	<.07	.23	<.01	.32	.71	3.33	.43
5.29	6	NT	NT	NT	NT	<.07	.22	.01	.47	<.07	.26	.01	.16	.60	3.57	.36
5.79	4	NT	NT	NT	NT	<.07	.84	.05	.62	<.07	.33	.01	.38	.57	2.52	.34
5.96	9	.14	1.03	.08	NT	<.07	.70	.04	.12	<.07	.43	.03	.12	.59	3.48	.43
11.40	5	NT	NT	NT	1.64	<.07	1.48	.14	.24	<.07	1.31	.15	.18	.55	3.02	.48
14.9	1	<.07	1.26	.09	.86	<.07	1.09	.16	.26	<.07	1.06	.10	.12	.81	3.66	.53

NT Not tested.
[1]Slags sulfated for 2 h with 10 wt pct Na_2SO_4 additive and subsequently leached with 1-wt-pct-HCl solution.
[2]Shown as oxide equivalents.

suitable conditions for leaching the sulfated slags. Of interest were (1) duration of leaching, (2) amount of leach liquor used (liquid-solid ratio), and (3) type of leach liquor. Slag from smelting test 3 was used.

Charge Preparation

Sulfated slag for these leaching tests was prepared in the following manner. The slag for the sulfation charge was blended with 10 wt pct Na_2SO_4 and 1 wt pct bentonite, and the blended constituents were pelletized with water on a disk pelletizer to form minus 10- plus 20-mesh pellets. The 200-g pelletized charge was reacted with equal proportions of SO_2 and O_2 at 800° C for more than 4 h. The sulfated slag was ground to pass through a 35-mesh screen prior to leaching.

Test Procedures

Five-gram portions of the sulfated slag were leached for periods of 5 to 60 min at ambient temperature in beakers. Either water or a 1-pct solution of HCl was used at liquid-solid ratios 10:1 and 20:1 by weight. After leaching, the slurry was filtered but not washed. The dried slag was sampled and analyzed to determine the percentage of solubles removed.

Results and Discussion

The effects of the various leaching conditions on impurity removals from sulfated slag are summarized in table 6.

TABLE 6. - Effect of various leaching conditions on impurity removal from sulfated slag[1]

Leach solution liquid-solid ratio	Leach time, min	Leached slag analysis, wt pct[2]				Impurity removal, pct			
		CaO	MgO	MnO	Na_2O	CaO	MgO	MnO	Na_2O
1 pct HCl:									
20:1	5	0.18	0.73	0.08	0.77	77.8	79.3	81.8	88.9
	10	.11	.68	.05	.53	86.8	81.4	87.9	92.7
	15	.11	.60	.05	.49	86.8	83.6	87.9	93.2
	30	<.07	.35	.04	.26	>92.3	91.0	91.7	96.6
	45	<.07	.22	.03	.18	>92.3	94.5	94.7	97.7
	60	<.07	.23	.03	.15	>92.3	94.0	94.7	98.1
10:1	5	.29	1.06	.09	1.08	62.9	69.1	78.0	84.0
	10	.21	.81	.05	.71	74.4	76.9	87.9	89.7
	15	.08	.65	.04	.40	90.2	82.3	90.9	94.4
	30	<.07	.38	.01	.20	>91.9	89.9	97.0	97.3
	45	<.07	.33	.01	.18	>91.9	91.3	97.0	97.9
	60	<.07	.35	.01	.19	>91.9	90.9	97.0	97.5
Water:									
20:1	5	.29	1.36	.08	1.05	72.7	70.6	86.4	88.4
	10	.15	.71	.04	.50	82.1	80.7	90.9	93.1
	15	.08	.53	.04	.54	90.2	85.8	91.7	92.6
	30	.08	.38	.03	.28	90.6	90.1	94.7	96.2
	45	<.07	.33	.03	.28	>92.3	91.5	94.7	96.3
	60	<.07	.16	.03	.16	>92.3	96.0	94.7	97.9
10:1	5	.25	.91	.06	.71	69.3	74.2	84.8	89.7
	10	.24	.83	.06	.70	71.0	76.7	84.8	89.9
	15	.18	.68	.05	.54	78.7	81.5	88.6	92.5
	30	.14	.53	.03	.30	83.8	85.8	93.9	96.0
	45	<.07	.50	.03	.16	>92.3	87.0	94.7	97.9
	60	<.07	.28	.03	.16	>92.3	92.7	94.7	97.9

[1]Slag derived from smelting test 3 contained, in wt pct, 0.85 CaO, 3.65 MgO, 0.44 MnO, and 2.30 Na_2O as pertinent constituents before sulfation.

[2]Shown as oxide equivalents.

The data indicate that excellent impurity removals were achieved from slag leached either in water alone or in a 1-wt-pct-HCl solution for at least 30 min.

An examination of the curves in figure 7 shows very little difference in the rate of impurity removal using different proportions and types of leach liquids. The utilization of a water leach at a liquid-solid ratio of 10:1 resulted in slightly lower removals of the Ca and Mg solubles, especially at times less than 45 min. The graphic data in figure 7 indicate that leaching the sulfated slag for a minimum of 30 min with either water or 1-pct HCl at a liquid-solid ratio of 20:1, or for 30 min with 1-pct HCl at a 10:1 liquid-solid ratio, would remove at least 90 pct of the impurities, including the promoter added.

From the standpoint of treating the waste streams of a potential large-scale operation, water would probably be preferred since the water liquor could be neutralized with limestone. Waste liquor of the water leach of sulfated slag exhibited a pH value of approximately 4.5. According to spectrographic data, the dissolved solids recovered from a sample of waste liquor from water leaching of slag consisted of >1 to 10 wt pct each of Ca, Mg, and Na; >0.1 to 1 wt pct each of Al, Fe, and Mn; 0.01 to 0.1 wt pct each of Si, Ti, and Zr; and 0.0001 to 0.001 wt pct Cu.

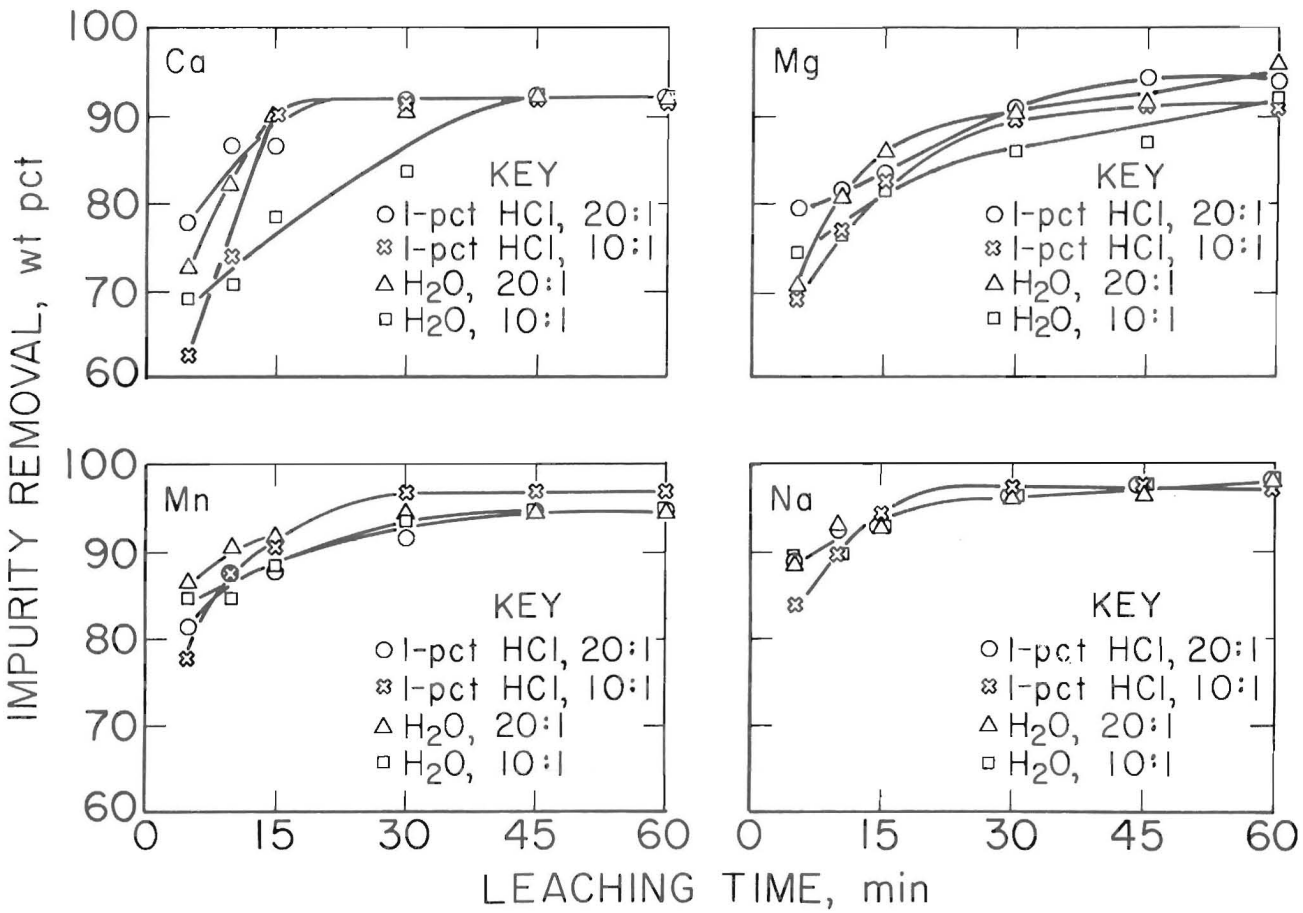

FIGURE 7. - Effect of various leaching conditions on impurity removal from sulfated slag 3 (table 2) containing 10 wt pct Na_2SO_4 additive.

PILOT PLANT STUDIES

PREPARATION OF TITANIUM SLAG

Ilmenite Concentrate

The ilmenite concentrate used in the pilot plant studies was the same as that used in the laboratory studies (table 1).

Equipment

The electric arc furnace employed to carbothermically reduce Tahawus ilmenite to separate iron and prepare low-iron titanium slag was described in a previous Bureau publication (7). Briefly, the three-phase ac, 1-st-capacity furnace was powered by a 1,000-kV·A transformer. The furnace was lined with carbon brick and a rammed carbon hearth rather than with a normal refractory material, such as magnesite, to prevent excessive contamination of the molten slag by refractory oxides. Carbon was considered a less objectionable impurity than refractory oxides in titanium slag.

Procedure and Results

The submerged-arc smelting procedure used by the Bureau differs somewhat from that used industrially to smelt ilmenite rock concentrate in Sorel, Canada, and ilmenite sand concentrate at Richards Bay in the Republic of South Africa. In industrial operations, 8 to 13 wt pct FeO is left in the slag to preserve bath fluidity and to facilitate tapping of the molten products from the furnace. In the Bureau smelting tests, less than 5 wt pct FeO was desired in the slag because the low-iron slag responded best to impurity removal by sulfation-leaching techniques.

To produce low-iron slag and still maintain bath fluidity, small amounts of soda ash were included in the furnace charges. The targeted FeO and Na_2O levels in the slag were about 5 wt pct for each constituent. Note that, in addition to its function as slag conditioner in the smelting step, the soda ash additive promoted the subsequent sulfation of the harmful slag impurities (8, 13). Without the promoter, only about 50 pct of the Ca, Mg, and Mn oxide constituents were sulfated (15). The Na_2O in the slag forms Na_2SO_4 in the sulfation step. Bench-scale tests showed that 5 wt pct Na_2O in titanium slag is sufficient promoter for impurity sulfation (8).

For submerged-arc smelting, a mixed carbon reductant consisting of 80 wt pct woodchips and 20 wt pct metallurgical-grade coke was used to ensure uniform flow of charge material into the molten pool and to maintain charge porosity, which aids in the escape of product gases from the furnace. The total carbon used to carbothermically reduce ilmenite charges was equivalent to 110 to 120 pct of stoichiometric requirements for the following chemical reactions:

$$FeO + C \rightarrow Fe + CO, \qquad (A)$$

and

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO. \qquad (B)$$

In addition, part of the carbon charge requirement was based on producing an iron product containing at least 2 wt pct C.

The experimental submerged-arc smelting procedure used in the present research was similar to that used and reported by previous Bureau investigators (7). Each of the six batch smelting tests was started with a small amount of charge material, free of woodchips, placed on the hearth to form a molten pool. After a satisfactory pool was formed by arcing on the initial charge material, the furnace was filled with a blended charge of ilmenite, woodchips, coke, and soda ash. Additional charge was added periodically to maintain a full furnace. During the test, bath samples were taken on a regular basis and analyzed to monitor the FeO and Na_2O levels in slag. The bath temperature was adjusted to between 1,625° and 1,675° C before the power was turned off and the products were tapped. Stream samples of the tapped iron metal and slag products were obtained for complete chemical analyses. The bath cooled too rapidly to

allow most of the quick-freezing slag to drain from the relatively small-scale furnace. The remaining slag was removed subsequently from the cooled furnace to assure smooth arc initiation on the hearth in the subsequent test. In industrial operations, where much larger electric arc furnaces are operated 24 h/d, the slag-freezing problem would be minimized. In the six tests, approximately 7.8 st of ilmenite concentrate was smelted to yield 4.4 st of low-iron slag and 2.5 st of iron products. Only 2.7 st of the slag was tapped; the other 1.7 st remained in the furnace. The frozen slag that was removed from the furnace hearth after each test by means of a jackhammer was not used in sulfation-leaching experiments because the product contained excessive amounts of carbon lining material.

The cooled, tapped slag product was crushed to minus 1/4 in, and the crushed material was subjected to magnetic separation to remove iron prills. The crushed slag was transferred to a rod mill and ground to pass through a 35-mesh screen. Approximately 2.5 st of clean, ground slag product, freed of iron prills, was recovered. The chemical data shown in table 7 indicate that approximately one-third of the titanium contained in the slag was as Ti_2O_3 with a 7-wt-pct combined level of pertinent CaO, MgO, and MnO impurities present.

Table 8 shows that the high-carbon iron product contained low levels of silicon and phosphorus, but the 0.25 wt pct S exceeded the maximum of 0.05 wt pct allowed in most commercial grades of pig iron. The sources of the S in the iron product were the ilmenite, which contained 0.7 wt pct S, and the carbon hearth lining, which contained 0.55 wt pct S. Oxidation of the ilmenite before smelting could help decrease the S level in the iron to an acceptable level.

TABLE 7. - Composition of 35-mesh, ground titanium slag smelted from Tahawus ilmenite

Constituent	wt pct
TiO_2	48.4
Ti_2O_3	25.5
FeO	5.0
MgO	5.5
CaO	.8
MnO	.7
Na_2O	5.5
Al_2O_3	3.9
SiO_2	4.0
S	.7

TABLE 8. - Composition of the iron product derived from Tahawus ilmenite concentrate

Constituent	wt pct
Fe	95.6
C	3.3
Ti	.5
Si	.1
P	.016
S	.25
Other	.1

SULFATION LEACHING OF TITANIUM SLAG

Background

Slag sulfation reactions are complex owing to the partitioning of the constituents between the various phases of the slag. The data shown in table 9 indicate that titanium slag is composed of three major phases--$Na_{0.23}TiO_2$, a pseudobrookite-type structure, and an Na-Mg-Al silicate--and six minor phases, including Mg-, Na-Ca-, and Ca-titanates. The pseudobrookite-type structure consists of black, acicular crystals that are embedded in a noncrystalline, silicate-type glass matrix. These orthorhombic crystals consist of oxides having the following chemical formulas (16): $(Fe^{2+}, Mg^{2+}, Mn^{2+}, Ti^{2+})O{\cdot}2TiO_2$ and/or $(Fe^{3+}, Al^{3+}, Ti^{3+})_2O_3{\cdot}TiO_2$. Titanium oxides form two solid-solution series with several constituents, including Al, Fe, Mg, and Mn, as illustrated by the formulas shown above. The above constituents, along with Ca, are partitioned in other phases, such as in titanates, as shown in table 9.

TABLE 9. - Phases present in titania-enriched slag smelted from Tahawus ilmenite using a soda ash additive, percent[1]

Phase	Phase in slag	Element								
		Na	Mg	Al	Si	S	Ca	Ti	Mn	Fe
$Na_{0.23}TiO_2$.....	10	6.8	0.9	0.4	<0.2	<0.5	0.9	52.0	<0.2	<0.2
Pseudobrookite.....	60	1.2	3.9	1.5	<.2	<.5	.2	52.0	.3	1.9
Na-Mg-Al silicate...	20	14.0	2.0	16.5	20.0	.5	<.2	1.3	.4	.3
Mg titanate.....	10	.7	11.5	.7	<.2	<.5	<.2	47.5	<.2	.2
Na-Ca titanate.....		11.2	<.5	<.4	<.2	<.5	22.5	31.2	<.2	<.2
Ca titanate.....		1.2	<.5	<.4	<.2	<.5	26.2	32.5	<.2	<.2
Fe prills.....		<.5	<.5	<.4	<.2	<.5	<.2	<.5	1.0	82.0
Mn-Fe sulfide.....		1.1	<.5	<.4	<.2	15.5	<.2	2.1	40.9	4.0
Na-Mn-Fe oxide.....		6.1	<.5	.8	1.2	3.0	<.2	<.5	28.0	26.0

[1]Phases determined by X-ray diffraction analyses; analyses by scanning electron microscopy using an energy-dispersive X-ray detector are normalized semiquantitative.

In the sulfation step, the Ca, Mg, Mn, and Na oxides in slag react selectively with SO_2 and O_2 to form water-soluble compounds that can be subsequently leached from the sulfated slag at ambient temperatures. Titanium and iron constituents do not react with SO_2 and O_2 to form stable sulfates at the temperatures used. Efficient sulfation of impurities in low-iron slags by SO_2-air or SO_2-O_2 mixtures is dependent upon the use of a promoter such as Na_2SO_4 (13, 15). The exact mechanisms by which the impurities are sulfated and the role of the sulfation promoter have not been established. In this investigation, the soda ash, which was added in the initial ilmenite smelting step to reduce the slag viscosity, served as the sulfation promoter. When the slag was sulfated, the Na constituent was converted to a soluble compound. Because Na, like Ca, Mg, and Mn, is an undesirable impurity in chlorination feedstock, the formulation of a leachable Na compound during slag sulfation was essential.

Use of low-iron slag is necessary to obtain maximum sulfation of slag. The impurities, if they remain in the pseudobrookite-type structure, do not respond to sulfation very well, as discussed later. Therefore, impurity sulfation is facilitated by the conversion of the pseudobrookite structure to rutile, which has a low solubility for impurities. Other Bureau investigators found that effective formation of rutile was not achieved in Sorel slag that contained 13.3 wt pct FeO, and 20 to 30 wt pct of the Ti remained as pseudobrookite (10).

Equipment

The main components of the continuous sulfation reactor, shown in figure 8, consist of a rotary kiln and a vertical-shaft furnace used to react a moving bed of slag with mixed SO_2 and air in a continuous operation. The nearly horizontal kiln consisted of a 5-ft-long, 4-in-ID stainless steel tube that rotated inside a tube furnace heated to 650° C by electric resistance elements. The kiln was used to partially oxidize and indurate the slag pellets before sulfation in the shaft furnace. The pellets were fed from a charge bin through a rotary valve into the kiln. An alumina-lined elbow was used to transfer the heated pellets to the sulfation reactor. The shaft-type reactor shown in figure 8 contained a 4-in-ID by 63-in-high vertical silicon carbide tube heated by two 2-ft-long electric elements. Thermocouples were spaced every 12 in along the outside wall of the reactor, with a thermocouple in the center of each section to control temperatures automatically. Metered flows of SO_2 and air entered the moving pellet bed below the heated section of the reactor. The reactor tube was surrounded by alumina blanket insulation contained within a shell. The sulfated product was discharged from the reactor by means of a screw-type apparatus. The product discharge unit was fitted with

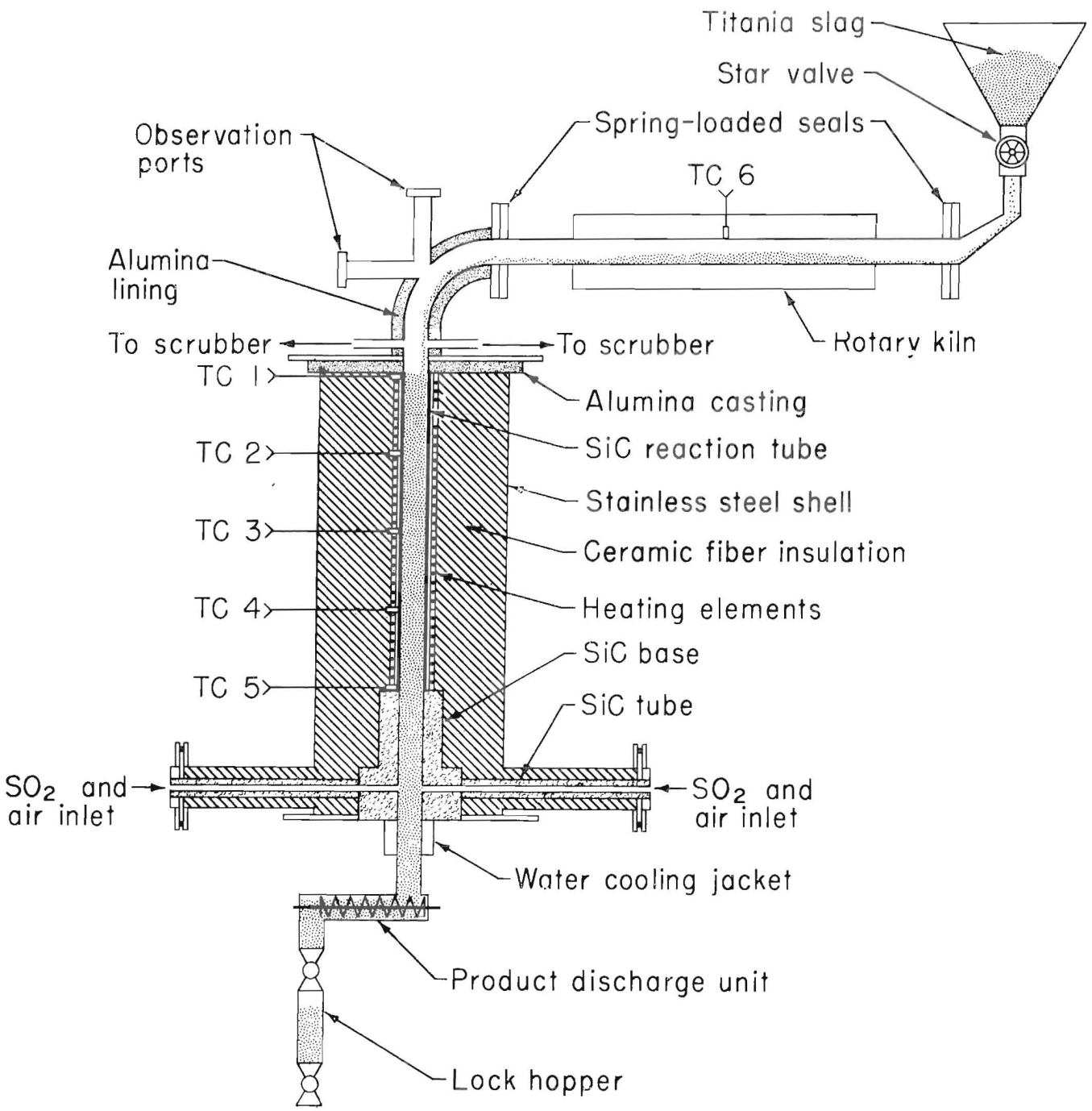

FIGURE 8. - Continuous slag sulfation reactor.

two valves in series so that the sulfated slag pellets could be removed for weighing and sampling without discharging SO_2 into the laboratory atmosphere. Moreover, the sulfation reactor was operated slightly below atmospheric pressure (5-in water column in a manometer) to minimize escape of SO_2 into the laboratory. Figure 9 shows the sulfation reactor and leaching sections of the pilot plant.

The leaching section of the pilot plant consisted of two 50-gal plastic tanks equipped with mechanical stirrers for water-leaching the soluble impurities from the ground, sulfated slag. A continuous bowl centrifuge (not shown in

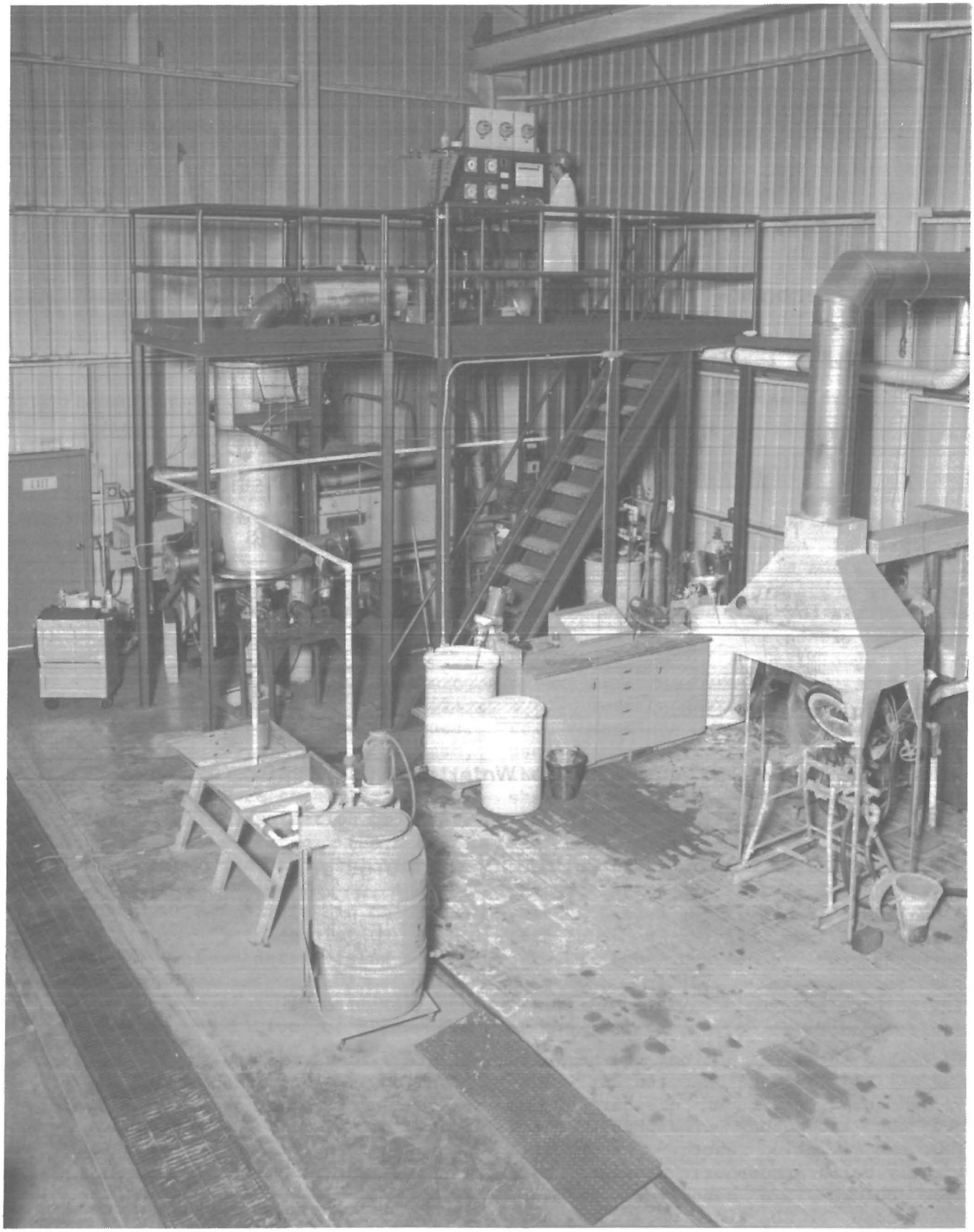

FIGURE 9. - Pilot plant used to sulfation-leach titanium slag.

figure 9) was employed to separate the leached solids from the liquor.

Pretreatment of Slag

Slag pretreatment consisted of pelletizing the ground material, drying the pellets, and oxidizing the dried pellets in a rotary kiln. The slag feed was pelletized in order to maintain a moving bed within the shaft-type furnace. Previous bench-scale tests showed that powdered slag charges sintered and formed solid compacts when sulfated. Accordingly, batches of 35-mesh ground slag blended with 2 wt pct bentonite clay and water were extruded in a laboratory pellet mill to form 3/8-in-diam by 5/8-in-long cylindrical pellets. The pellets were dried in an oven at 150° C for at least 24 h before sulfation. The dried pellets were screened to remove the minus 35-mesh fines before charging the material into the kiln. The slag fines caused sticking and agglomeration of the pellets in the moving bed and eventual plugging of the reactor.

Slag oxidation was found necessary to minimize the temperature buildup of pellets undergoing subsequent sulfation in the moving bed. The dried pellets were fed into the rotary kiln and oxidized with an O_2 flow equivalent to 0.23 ft^3/min for each 0.17 lb of slag. The following oxidation reactions were assumed to occur in the kiln:

$$C + O_2 \rightarrow CO_2, \qquad (C)$$

$$FeO + 1/4O_2 \rightarrow 1/2Fe_2O_3, \qquad (D)$$

and

$$Ti_2O_3 + 1/2O_2 \rightarrow 2TiO_2. \qquad (E)$$

Approximately 40 pct of the total heat of reaction generated by the oxidation and sulfation of slag pellets is derived from the oxidation of C, FeO, and Ti_2O_3 constituents.

Sulfation of Slag

Because material and time constraints prevented the use of a full factorial test design, only a limited number of tests using a two-level, three-variable, partial factorial design (17) were made to obtain the best possible conditions for sulfating the slag. This test design was based on a simple cube whose edges were defined by the operating ranges of the three independent variables. The region then was investigated by obtaining data at values representing the centroid and the corners of the cube (17).

The following ranges of operating conditions were investigated to continuously sulfate slag in pilot plant tests: slag feedrates of 10, 15, or 20 lb/h; SO_2 quantities of 150, 200, and 250 pct of stoichiometric amounts required to selectively sulfate the CaO, MgO, MnO, and Na_2O constituents in slag; and reactor operating temperatures of 750°, 800°, and 850° C.

A typical sulfation test lasted 7 to 9 h and was conducted as follows: The sulfation reactor was charged with approximately 70 lb of pellets during preheating of the apparatus to a predetermined operating temperature. A moving bed was established by starting the slag feeder and prodcut discharge units. Bed height was kept constant and was monitored closely by visual observations made through a sight glass mounted in the elbow section between the rotary kiln and the reactor. After the apparatus was preheated for about 1 h, metered flows of SO_2 and air were introduced into the reactor. The reactant-gas ratio used in the sulfation reactor consisted of 1 part SO_2 for each 0.5 part O_2 by volume. Residence times of the pellets at the 10- and 20-lb/h slag feedrates were 3.7 and 1.8 h, respectively.

Samples of the sulfated product stream were taken every 1/2 h for chemical analyses, especially for sulfur content and for bench-scale leaching to determine the percentage of impurities solubilized. The residual impurity levels in the leached samples were used to determine the effectiveness of sulfation.

Leaching of Sulfated Slag

The stream samples of sulfated pellets taken periodically during the pilot tests were ground and leached separately to determine the effects of sulfation condi-

tions on the ease of removal of soluble impurities. In addition, a 100-lb composited sample of sulfated pellets from the four tests made at a 10-lb/h slag feedrate was leached in larger scale equipment to obtain sufficient product for evaluation in a laboratory fluidized-bed chlorinator.

Bench Scale

Previous tests established that the sulfated pellets could be leached either in water alone or in dilute HCl solution at ambient temperatures to remove the soluble impurities. Data indicated that the solubilities of $CaSO_4$ in water and in 1-wt-pct-HCl solution were 2 g/L and about 7 g/L, respectively.

The stream samples were leached in 1-wt-pct-HCl solution to obtain stable samples of leach liquor for chemical analyses. Liquor from water leaching exhibited a tendency to form precipitates before being analyzed owing to hydrolysis reactions. It was necessary to acidify the liquor samples of water leaching to prevent precipitates from forming. Accordingly, the stream samples were ground and 5-g portions of this material were leached using 10 parts HCl solution for each part slag in stirred slurries at ambient temperature for 1 h. The slurries were filtered and the solids repulped with HCl solution for 5 min. After filtering, the solids were dried and chemically analyzed for impurity contents.

Large Scale

A 100-lb sample of composited slag pellets was ground to pass through a minus 35-mesh screen to prepare fine material for leaching. The ground material was leached in water in 50-gal plastic tanks using 10 parts water for each part slag by weight. Water, rather than HCl solution, was used to avoid handling of corrosive solutions in the available equipment. The mechanically stirred slurries were leached for 1 h before transfer to a horizontal-bowl, continuous centrifuge where the solids were separated from the liquor. The solids were repulped with fresh water, and the slurries were pumped through the centrifuge to separate the wash water. In actual industrial practice, the leach slurry probably would be pumped to a rotary vacuum-drum filter to separate and wash the solids. With such a rotary filter, the liquor-to-solids ratio used in the leaching step could be decreased from 10:1 to 5:1. The large batch of leached slag was dried in an oven at 150° C and sampled for chemical and X-ray diffraction analyses.

The liquor from the large-scale leach of sulfated pellets exhibited a pH of 3.5. To analyze the elements in the dissolved solids, a sample of liquor was evaporated to dryness. Spectrographic data indicated that the solids consisted of >1 to 100 pct each of Ca, Mg, and Na; >0.1 to 1 pct each of Fe, Mn, and Al; >0.01 to 0.1 pct each of Ti and Zr; >0.001 to 0.01 pct Ni; and 0.0001 to 0.001 pct Cu. The liquor was neutralized with ground limestone and the resultant slurry was filtered to separate the precipitate, which consisted mainly of $CaSO_4$ with small amounts of Fe, Mn, Al, Si, Ti, and Zr.

Results and Discussion

The two major titanium-bearing phases, sodium titanate ($Na_{0.23}TiO_2$) and a pseudobrookite-type structure, were essentially converted to rutile in the sulfated stream samples. X-ray diffraction and SEM data indicated that the sulfated pellets contained rutile as a primary phase (40 to 100 pct), with pseudobrookite-type structure and $CaSO_4 \cdot 3MgSO_4$ as minor phases (5 to 30 pct) and anatase as a barely detectable phase (<1 pct). In addition, a noncrystalline, silicate-type glass phase containing Al, Si, Fe, Mg, Mn, Ti, Na, and S was present. Neither Mg or Mn was found in the rutile phase. Sulfur scans made of mounted specimens of sulfated pellets revealed that only trace amounts of S were in the pseudobrookite-type phase containing Mg and Mn constituents. Apparently these constituents did not respond to sulfation when in the pseudobrookite-type structure. For this reason, maximum conversion of the above structure to rutile is desired to achieve effective formation of soluble Mg and Mn compounds.

Table 10 shows the impurity contents of leached stream samples sulfated in the range of the three selected variables. The data indicate that the leached slags sulfated at the rate of 10 lb/h contained the lowest level of harmful impurities. The total impurity levels of the leached samples increased from 1.8 to 3.2 wt pct as the slag feedrate increased from 10 to 20 lb/h. All the leached samples contained less than 0.2 wt pct CaO. The higher MgO levels of 1.5 to 2.8 wt pct indicate Mg was more difficult to remove than CaO. The effects of sulfation conditions on the MgO levels in the leached samples can be seen rapidly in the cube diagram of figure 10.

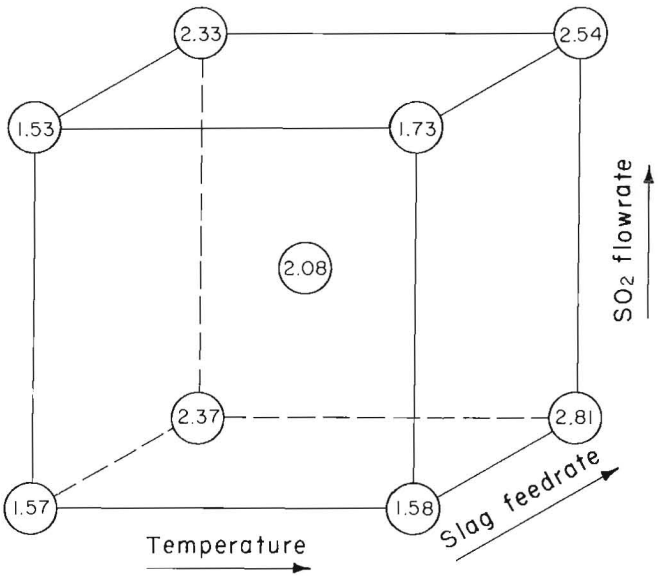

FIGURE 10. - MgO level in leached slag samples as a function of sulfation conditions.

The chemical composition of the large batch of leached slag is shown in table 11. The leached product contained 1.3 wt pct MgO, which is slightly lower than an average of 1.6 wt pct MgO contained in the stream samples of leached slag at the 10-lb/h feedrate in table 10. The small difference in MgO content is believed to be due to the larger scale of leaching used.

The sulfation-leached slag containing 85.5 wt pct TiO_2, with 0.07 wt pct CaO, 1.3 wt pct MgO, and 0.2 wt pct MnO, was comparable to the industrially produced Richards Bay slag, which contained 85.5 wt pct TiO_2, with 0.14 wt pct CaO, 0.9 wt pct MgO, and 1.4 wt pct MnO impurities. As mentioned previously, Richards Bay slag is reported to be suitable chlorination feedstock.

X-ray data indicated that the large batch of leached slag contained rutile as a primary phase (40 to 100 pct), anatase as a minor phase (5 to 30 pct), and pseudobrookite-type structure and cristobalite as barely detectable phases (<1 pct).

TABLE 10. - Effect of sulfation conditions on pertinent impurity levels in leached slag samples[1]

Sulfation conditions			Impurity level in sulfation-leached slag samples, wt pct[2]			
Slag feed, lb/h	SO_2, pct of stoichiometric[3]	Reactor preheat temp, °C	CaO	MgO	MnO	Total
10	150	750	0.07	1.57	0.18	1.82
10	250	750	.07	1.53	.18	1.78
10	150	850	.07	1.58	.17	1.82
10	250	850	.13	1.72	.19	2.04
15	200	800	.09	2.08	.25	2.42
20	150	750	.10	2.37	.29	2.76
20	250	750	.07	2.33	.30	2.70
20	150	850	.07	2.81	.35	3.23
20	250	850	.07	2.54	.30	2.91

[1]50-g stream samples of the sulfated pellets from each test were water-leached in beakers, and the resultant slurries filtered.

[2]Impurity levels in untreated slag feed were, in wt pct, 0.84 CaO, 5.5 MgO, 0.66 MnO, and 7.0 total.

[3]SO_2 stoichiometry is based on sulfation of the CaO, MgO, MnO, and Na_2O constituents in the slag.

TABLE 11. - Composition of sulfation-leached titanium slag from pilot plant tests[1]

Constituent	wt pct
TiO_2	85.5
CaO	.07
MgO	1.3
MnO	.2
Al_2O_3	3.4
SiO_2	4.6
Fe_2O_3	4.3
S	.26
Na_2O	.2

[1]Composited slag derived from 4 tests made at the 10-lb/h feedrate of slag; the slag contained 5.6 wt pct S before leaching. A 100-lb batch of the slag was water-leached in larger tanks, and the resultant slurries were pumped to a continuous centrifuge to separate the leached slag from the liquor.

The results obtained with the shaft-type reactor, in which the pellets flowed downward by means of gravity, are quite encouraging since this was the initial attempt to continuously sulfate slag in larger scale equipment. In previous bench tests, the slag pellets were sulfated in a static-bed reactor without any indications of temperature increase due to exothermic reactions. In the pilot reactor, control of reaction temperatures in the moving pellet bed was not satisfactory at times. The maximum temperature in the bed sometimes exceeded the temperature set by the instruments controlling the reaction zone heaters by more than 100° C. Excessive bed temperatures would influence the thermal stability of $MgSO_4$, as well as cause pore closure within the individual pellets. Thus, the reactant gases, SO_2 and air, would be unable to diffuse into the slag pellets.

Further scale-up of the sulfation technique to an industrial-sized operation would require significant changes in equipment design and operating procedures. A vertical-shaft-type furnace with a silicon carbide lining and an air-cooled shell would help reduce the problems with temperature control in the moving-pellet bed. Use of reactant gas mixtures with lower SO_2 concentrations would decrease the sulfation rate, thereby reducing the generation of heat. Another suggested change is to add the reactant gases at various locations in the bed rather than at the bottom of the bed, as practiced in the pilot sulfation reactor. This change would increase the size of the reaction zone in the moving bed, where most of the slag sulfation occurs.

CHLORINATION OF SULFATION-LEACHED SLAG

Samples of the sulfation-leached titanium slag shown in table 11 were found amendable to continuous chlorination in a laboratory fluidized-bed reactor used to produce $TiCl_4$. In 5-h tests, no evidence of loss of fluidization caused by liquid metal chloride impurities agglomerating the slag and coke particles in the bed was noted. However, extended periods of operation are required to assure the suitability of the slag as chlorination feedstock.

The fluidized-bed tests were performed in a 2-in-diam, 42-in-high quartz tube reactor. The experimental procedure entailed continuously feeding titanium slag into the top of the bed and introducing chlorine in the bottom. Approximately 400 g of minus 65-mesh petroleum coke was charged prior to feeding slag into the reactor. The fluidized bed of coke was heated to a reaction temperature of 950° C, as measured by a thermocouple inserted inside the reactor. The slag was fed at a rate averaging 5 g/min by means of a variable-speed screw feeder. Argon at a rate of 3.2 L/min was fed with the slag to prevent metal chloride vapors from entering and condensing in the slag feed line. Chlorine flow averaged 3.2 L/min. The $TiCl_4$ product was collected in two water-cooled condensers located downstream from the reactor. In these tests, total conversion of TiO_2 in titanium slag to $TiCl_4$ generally exceeded 93 pct.

CONCLUSIONS

Results of bench-scale tests show the sulfation-leaching method effectively treats titanium slags made from a low-grade ilmenite concentrate. Efficient conversion of the harmful CaO, MgO, and MnO impurities in slag by SO_2-O_2 mixtures to leachable compounds is dependent on FeO content of slag, use of a sulfation promoter, temperature, and time. Slags that contained 5.96 wt pct or less FeO responded the best to sulfation at temperatures of 800° C and above in the presence of Na_2SO_4 promoter. At 900° C, reaction times of less than 15 min are sufficient to convert the Ca and Na compounds to soluble form, while 2 h is required for Mn. Magnesium proved to be the most difficult of the impurities to sulfate in slag.

Leaching studies show that the soluble compounds were readily removed from sulfated slag leached in water alone or dilute hydrochloric acid solutions at ambient temperatures for at least 30 min. More than 90 pct of the undesirable impurities, including the additive used as a sulfation promoter, were removed from the leached slags to yield products of suitable grade for chlorination purposes.

In pilot plant tests, response of pelletized slag to sulfation by SO_2-air mixtures in a shaft furnace depended on reactor residence time. Oxidation of the slag in an adjacent rotary kiln before sulfation helped reduce the heat buildup in the moving pellet bed, but further improvements in operating procedures are needed. Following sulfation, the sulfated Ca, Mg, and Mn impurities were readily leached from ground slag in water.

A leached slag product that contained 85.5 wt pct TiO_2 with troublesome impurity levels reduced to 1.86 wt pct was obtained. The slag upgraded in the pilot plant investigation was essentially equal in grade to the Richards Bay slag made commercially from ilmenite sand concentrate in the Republic of South Africa. Tests made in a laboratory fluidized-bed chlorinator demonstrated that the sulfation-leached slag was amenable to continuous chlorination without the harmful liquid metal chloride impurities defluidizing the bed.

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